

A facile synthesis and the asymmetric catalytic activity of BINOL-based thiazole (thiadiazole) thioether ligands

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Abstract

Four new BINOL-based thiazole (thiadiazole) thioether ligands (*S*-1), (*S*-2), (*S,S*-3) and (*S*-4) were prepared. When their catalytic effectiveness was tested, good results (up to 93% ee and 97% yield) were obtained in the asymmetric addition of diethylzinc to aldehydes while poor results were obtained in the asymmetric conjugate addition of diethylzinc to enones.

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1. Introduction

In catalytic asymmetric systems, small changes in the donating ability of a ligand or the size of a substituent can have dramatic effect on the catalytic efficiency and enantioselectivity [1]. 1,1'-Binaphthol (BINOL) is one of the most effective chiral ligands in asymmetric catalysis [2]. Substituents at the 3-position of BINOL are normally introduced via a two-step protocol that involves treatment of a suitably protected BINOL with an organolithium reagent, followed by reaction with an electrophile [3]. BINOL ligands substituted by the introduction of heteroaromatic groups at the 3 or 3,3'-positions are less reported [4]. In our previous research, some nitrogen-contained aromatic heterocycle groups such as 1,3,5-triazin-2-yl, 2-quinolyl and 1,2,4-triazol-1-ylmethyl were, respectively, introduced to the 3 or 3,3'-positions of BINOL, and their catalytic applicability in the addition of diethylzinc to aldehydes was also reported [5].

In recent years, chiral S-donor ligands have proved to be useful as other classical asymmetric ligands, especially

when combined with other donor atoms [6]. Despite of the vast knowledge on sulfur-metal interactions in coordination chemistry [7], the use of chiral BINOL ligands containing sulfur atoms in asymmetric catalysis appears to be still rather undeveloped. Sulfur has somewhat less donor and acceptor character. In addition to this electronic consideration, the sulfur atom, in thioether ligands, for example, has only two substituents which can create a less hindered environment. Woodward [8] developed copper-catalyzed asymmetric conjugate additions of various organometallic reagents to linear enones in the presence of sulfur-containing BINOL ligands, and the sulfur atom proved to be necessary in this reaction. Kang [9] reported some BINOL-based ligands containing sulfur were effective in promoting 1,4-additions of organometallics to various enones. To the best of our knowledge, BINOL-based ligands bounded with both sulfur-contained heterocycle (thiazole or thiadiazole) and thioether block in which the sulfur might serve as a talent anchor have never been reported. Therefore, it should be of interest to explore the catalytic ability of this kind of BINOL ligands. Herein, we report the synthesis of new chiral ligands (*S*-3-(5-methyl-1,3,4-thiadiazol-2-ylthio)methyl-BINOL [(*S*-1)], (*S*-3-(benzothiazol-2-ylthio)methyl-BINOL [(*S*-2)], (*S,S*-2,5-bis(2,2'-dihydroxy-1,1'-binaphthalen-3-yl)-1,3,4-thiadiazole [(*S,S*-3)], and (*S*-3,3'-bis[(5-methyl-1,3,4-thiadiazol-

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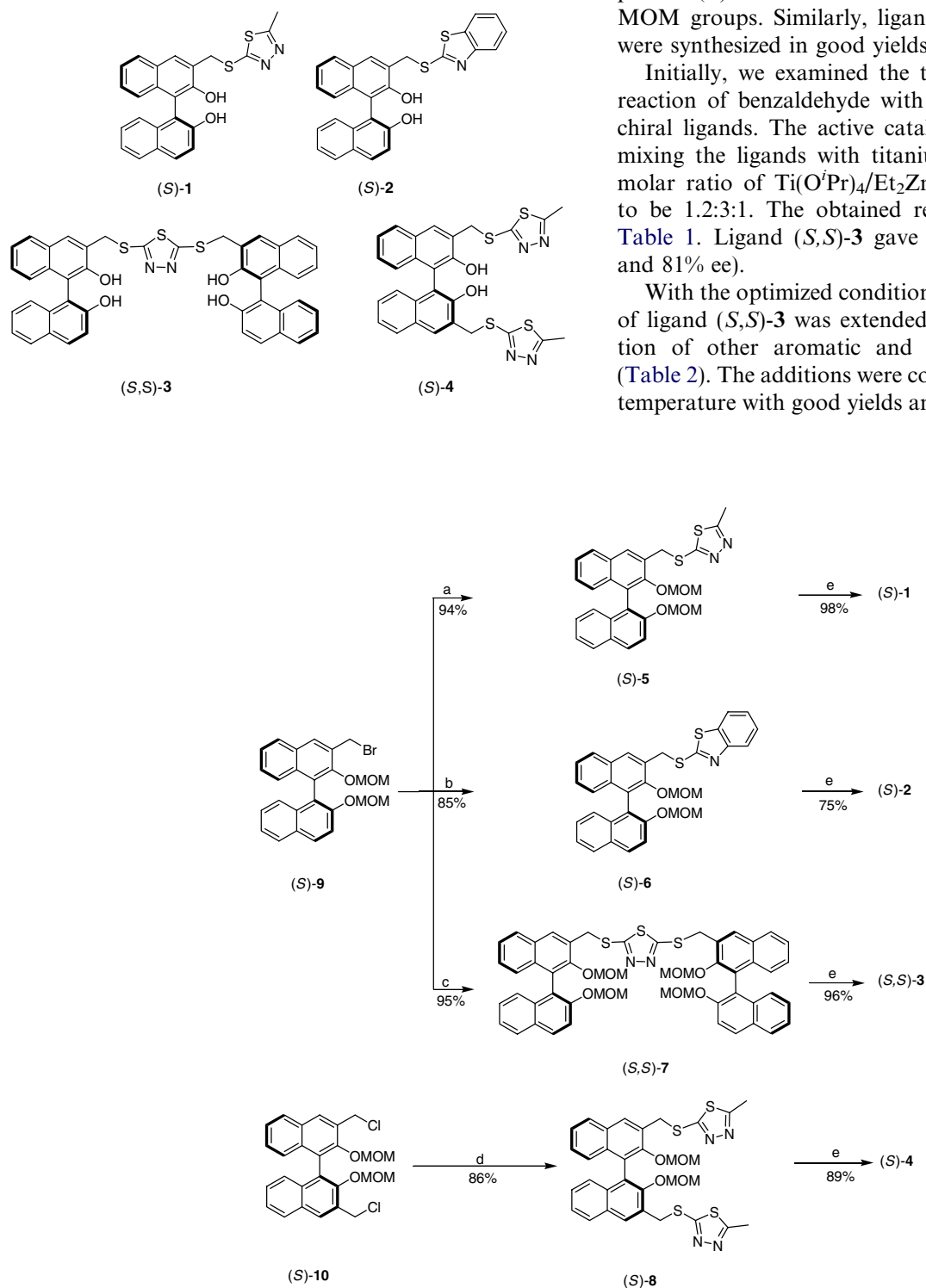
2-ylthio)methyl]-BINOL [(*S*)-**4**] and their application in asymmetric addition of diethylzinc to aldehydes in the presence of titanium tetraisopropoxide and in asymmetric conjugate addition of diethylzinc to enones in the presence of $\text{Cu}(\text{OTf})_2$.

2. Results and discussion

The synthetic route for ligands (*S*)-**1**, (*S*)-**2**, (*S,S*)-**3** and (*S*)-**4** is outlined in Scheme 1. (*S*)-**5** was easily prepared by the reaction of (*S*)-**9** with 2-mercapto-5-methyl-1,3,4-thiadiazole in high yield, and the corresponding target compound (*S*)-**1** was obtained after deprotection of the MOM groups. Similarly, ligands (*S*)-**2**, (*S,S*)-**3** and (*S*)-**4** were synthesized in good yields.

Initially, we examined the titanium-catalyzed addition reaction of benzaldehyde with diethylzinc using the four chiral ligands. The active catalyst was formed *in situ* by mixing the ligands with titanium tetraisopropoxide. The molar ratio of $\text{Ti}(\text{O}^i\text{Pr})_4/\text{Et}_2\text{Zn}/\text{benzaldehyde}$ was set up to be 1.2:3:1. The obtained results were summarized in Table 1. Ligand (*S,S*)-**3** gave the best result (95% yield and 81% ee).

With the optimized conditions for benzaldehyde, the use of ligand (*S,S*)-**3** was extended to the asymmetric ethylation of other aromatic and α,β -unsaturated aldehydes (Table 2). The additions were completed within 5 h at room temperature with good yields and ee values for all the alde-



Scheme 1. Synthesis of (*S*)-**1**, (*S*)-**2**, (*S,S*)-**3** and (*S*)-**4**. Reagents and conditions: (a) 1 equiv 2-mercapto-5-methyl-1,3,4-thiadiazole, KOH, reflux for 2 h; (b) 1 equiv 2-mercaptobenzothiazole, KOH, reflux for 2 h; (c) 0.5 equiv 2, 5-dimercapto-1,3,4-thiadiazole, KOH, reflux for 2 h; (d) 2 equiv 2-mercapto-5-methyl-1,3,4-thiadiazole, KOH, reflux for 2 h; (e) CH_2Cl_2 , CH_3OH , 6 M HCl, r.t.

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